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Boranes

The Propargyl Rearrangement to Functionalised Allyl-Boron and Borocation Compounds

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Abstract: A diverse range of Lewis acidic alkyl, vinyl and aryl boranes and borenium compounds that are capable of new carbon–carbon bond formation through selective migratory group transfer have been synthesised. Utilising a series of heteroleptic boranes [PhB(C₆F₅)₂ (**1**), PhCH₂CH₂B(C₆F₅)₂ (**2**), and E-B(C₆F₅)₂(C₆F₅)C≡C(l)R (R = Ph **3a**, nBu **3b**)] and borenium cations [phenylquinolotoborenium cation ([QOBPh]

[AlCl₄], **4**], it has been shown that these boron-based compounds are capable of producing novel allyl- boron and boronium compounds through complex rearrangement reactions with various propargyl esters and carbamates. These reactions yield highly functionalised, synthetically useful boron substituted organic compounds with substantial molecular complexity in a one-pot reaction.

Introduction

For many years the chemistry of boron compounds has played an important role in synthetic organic and inorganic chemistry, reflected by the award of several Nobel prizes in chemistry. The use of boronic acids in industry for Suzuki cross-coupling reactions is critical for the preparation of a range of compounds, such as poly-olefins and styrene derivatives, and is used for the synthesis of pharmaceuticals and speciality chemicals,^[1] whereas a range of boron hydrides have applications in reduction and hydroboration reactions.^[2] In addition, the inherent Lewis acidity of electron deficient Group 13 compounds has led to their broad application as Lewis acid catalysts.^[3,4] Related to this, Lewis acidic boranes, such as B(C₆F₅)₃,^[5] have found widespread applications in catalysis (such as in frustrated Lewis pair (FLP) hydrogenation^[6] and hydrosilylation^[7] reactions) as well as in 1,1-carboboration reactions.^[8] Traditionally, 'activated' alkynes were employed in such synthetic methodologies, for example, in the systems introduced by Wrackmeyer et al. whereby acetylide moieties were functionalised with heavier Group 14 metals (i.e., silyl, germyl, stannyl or plumblyl

groups).^[9] More recently, work by Erker et al. has furthered this research by applying such transformations to 'normal' or unactivated terminal and internal alkynes with B(C₆F₅)₃, generating vinyl boranes.^[8,10]

Borocations have recently emerged as comparable alternatives to B(C₆F₅)₃, whereby the Lewis acid possesses a formal positive charge, enhancing the Lewis acidity of the boron centre.^[11] It has been shown previously that a variety of these three-coordinate borocations (borenium cations) have been employed in borylation^[12] reactions including haloboration^[13] and 1,*n*-carboboration.^[14,15] The latter involve the addition of R-[B] to a π -bond, and present a selective migratory aptitude of the R-group from boron to carbon.^[14] In addition, borenium cations have recently been found to act as the Lewis-acid component of FLPs for hydrogenation reactions and can offer superior catalytic activity compared to neutral borane Lewis acids.^[16]

In this context, our recent studies have probed how B(C₆F₅)₃ can mimic established precious metal (Au^I) catalysts in intramolecular alkyne activation^[17] in the metal-free, catalytic synthesis of oxazoles.^[18] Although these studies reveal that B(C₆F₅)₃ is a powerful reagent to facilitate organic transformations, we have also shown that B(C₆F₅)₃ exhibits a propensity to undergo C₆F₅ group migration (as also observed in 1,1-carboboration reactions by Erker *inter alia*).^[8] which has led to a family of allylboron compounds that are themselves extremely versatile reagents in organic synthesis.^[19] Traditional routes to allylation reagents rely upon the hydroboration of alkenes, transition-metal-catalysed borylation of allylic compounds or the addition of reactive s-block metal allyl reagents to a borinic or boric ester.^[20] However, our approach, using the propargyl rearrangement, allows a unique method for generating allyl-boron reagents that demonstrates an atom-economic solution. Currently however, our approach has been limited to the use of the homoleptic highly Lewis-acidic borane B(C₆F₅)₃, which

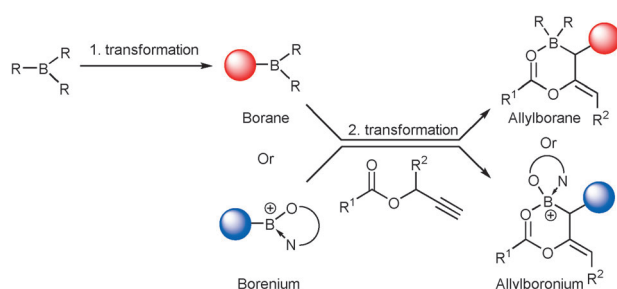
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severely confines the scope of these reactions to the generation of allyl boron compounds with incorporation of C_6F_5 -groups only. Approaches to expand the library of reagents are critical to fully exploit this potential reactivity pathway in organic synthesis. In this work, we reveal a novel methodology for the formation of a series of densely functionalised allylboron compounds with synthetic ease, in which we incorporate a variety of synthetically useful, transferable groups other than simply ' C_6F_5 ' units. Thus, the elucidation of the diverse chemistry involved with the newly established propargyl rearrangement reaction through the use of a series of heteroleptic boranes and borenium compounds is explored here (Scheme 1).



Scheme 1. This work: tandem synthesis of B–C bonds to novel boranes and borocations.

Results and Discussion

The starting point of this project was the preparation of a library of electrophilic boron compounds that are by nature Lewis acidic but also contain a “transferable” R-group (Scheme 2).^[10b,21] To maintain high Lewis acidity at boron, which is important in the propargyl rearrangement, compounds of the type $RB(C_6F_5)_2$ and borocations were selected as target boron Lewis acids. The boron Lewis acid derivative $PhB(C_6F_5)_2$ (**1**)^[22] was prepared from salt metathesis of $PhBCl_2$ and LiC_6F_5 ,^[23] whereas $PhCH_2CH_2B(C_6F_5)_2$ (**2**)^[24,25] was prepared

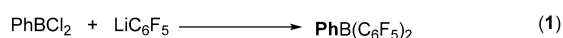
from the 1,2-hydroboration of styrene using Piers’ borane, $HB(C_6F_5)_2$, using literature procedures.^[24,26]

Novel 1,1-carbaboration reactions of iodoalkynes, $R-C\equiv C-I$ ($R=Ph, nBu$) using $B(C_6F_5)_3$ were found to proceed rapidly with excellent selectivity, yielding the iodoalkenylborane products (**3a,b**) within 10 min at room temperature in quantitative yields in $CDCl_3$ (Scheme 2; for experimental details, see the Supporting Information). Importantly, the incorporation of a halogen into the borane offers a functional handle for subsequent reactivity. Indeed, the products of these reactions are vinyl iodides, which are instrumental in new C–C bond-forming reactions, showing particular promise with a breadth of specialties from routine laboratory protocols to the production of natural products and drug molecules (e.g., through Sonogashira or Suzuki coupling or through the Heck reaction).^[27] Notably, phenyl iodoalkyne ($Ph-C\equiv C-I$) reacted with $B(C_6F_5)_3$ to produce the product with very high stereoselectivity (ca. 98:2 *E/Z*) of the product **3a** as determined by in situ multinuclear NMR spectroscopy, whereas the butyl derivative ($nBu-C\equiv C-I$) was slightly less selective, giving a mixture of *E/Z* isomers of the product **3b** in an approximate 80:20 ratio. This high selectivity for one isomer is in contrast to that observed previously with “normal” terminal alkynes, that is, alkyl/aryl substituents, where an approximate 1:1 ratio of *E/Z* isomers is formed.^[25] This 1,1-carbaboration product was further evidenced when observing the ^{19}F NMR spectra; both **3a** and **3b** produced resonances for the fluorine atoms in the *ortho* ($\delta = ca. -127.0$ (4F), -137.5 (2F) ppm), *para* ($\delta = ca. -144.5$ (2F), -152.6 (1F) ppm) and *meta* ($\delta = ca. -160.5$ (6F) ppm) positions, clearly showing the migration of one perfluorophenyl fragment. Minor artefacts observed in the ^{19}F NMR spectra of **3b** can be assigned to the minor stereoisomer formed during the rearrangement step. Supporting ^{11}B NMR spectra show a single broad resonance for **3a** at $\delta = 57.9$ ppm, with **3b** showing a similar broad major peak at $\delta = 58.4$ ppm consistent with other 1,1-carbaboration products.^[8] Attempts to obtain the single stereoisomer from the *E/Z* mixture of **3b** through irradiation with UV light (HPK 125, pyrex filter)^[25] proved unfruitful, with a composite spectrum still remaining post exposure.

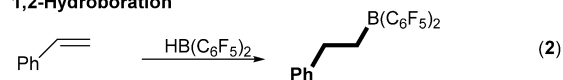
By introducing a formal positive charge at boron, the necessity to employ fluorinated substituents to retain a highly Lewis-acidic centre is unnecessary. Capitalising on this, we synthesised borenium compound **4** ($[QOBPh][AlCl_4]$) from the reaction of TMS-protected 8-hydroxyquinoline (QOH) with $PhBCl_2$, followed by addition of $AlCl_3$. Compound **4** has recently been reported by Ingleson with successful employment in carboboration reactions with terminal alkynes, featuring exclusive transfer of the phenyl group.^[14]

The borane and borenium compounds synthesised above were then tested as alkyl, vinyl and aryl transfer reagents in the propargyl rearrangement reaction, which to date has only been investigated using $B(C_6F_5)_3$ (Scheme 3).^[19] The heteroleptic boranes (**1–3**) synthesised here would be expected to undergo selective transfer of the more electron-rich substituent, as seen in 1,1-carbaboration reactions reported by Erker and Ingleson inter alia.^[8,10,14] A series of propargylic substrates (**5a–h**) were synthesised, including propargyl esters and carba-

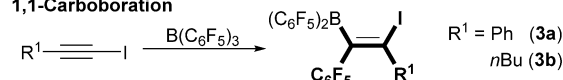
Salt Metathesis



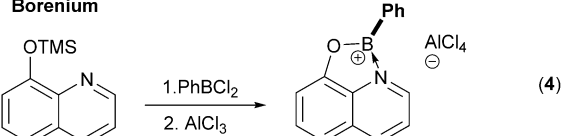
1,2-Hydroboration



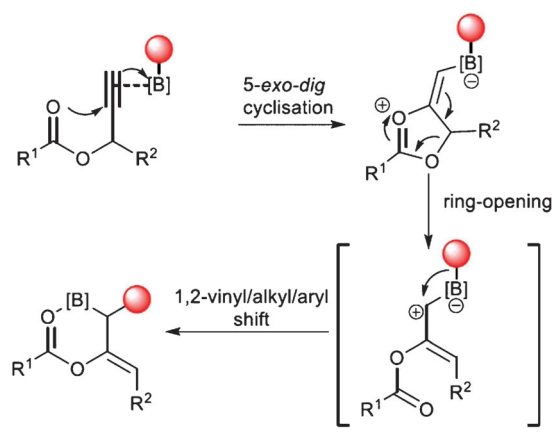
1,1-Carbaboration



Borenium



Scheme 2. Highly electrophilic borane and borenium Lewis acids.



| Substrate | R ¹ | R ² |
|-----------|---|----------------|
| 5a | Ph | H |
| 5b | <i>p</i> -MeC ₆ H ₄ | H |
| 5c | <i>p</i> -OMeC ₆ H ₄ | H |
| 5d | <i>p</i> -NO ₂ C ₆ H ₄ | H |
| 5e | Ph | Me |
| 5f | <i>p</i> -MeC ₆ H ₄ | Me |
| 5g | Me | Me |
| 5h | Ph ₂ N | H |

Figure 1. The propargyl rearrangement with boranes and borenium cations (top), and propargyl substrates tested (bottom).

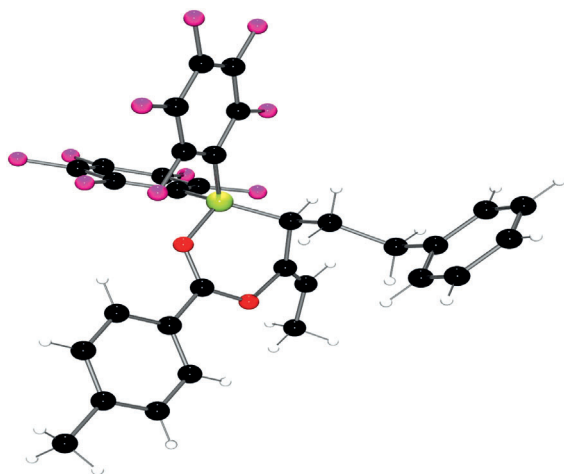
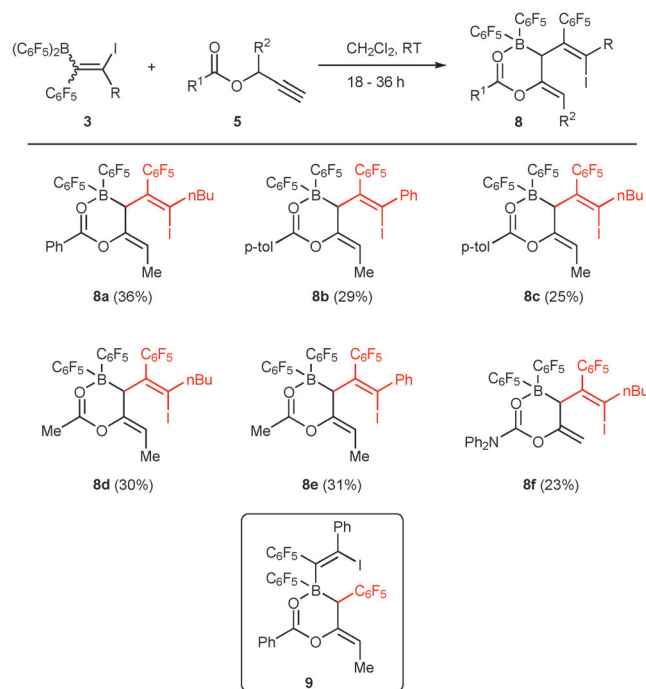


Figure 2. Solid-state structure of **6**. C: black, H: white, O: red, B: yellow-green, F: pink.

mates (Figure 1). Initially, PhB(C₆F₅)₂ (**1**) was reacted with the propargyl ester **5f** in a 1:1 stoichiometric ratio. Unfortunately, the desired migration of the more electron rich phenyl group over the pentafluorophenyl group was found to not occur exclusively, instead giving a mixture that mainly consisted of three products resulting from unselective aryl group transfer (See supporting information).



Scheme 3. Rearrangement products (**8a-f**) from vinyl group transfer. Insert (**9**) shows minor product from C₆F₅-migration. Yields indicated are isolated yields.

Similar results were observed when substituting the phenyl group for an ethylbenzene group (-CH₂CH₂Ph). The reaction of borane **2** with **5f** also gave unselective R-group transfer, indicating that the lability of the alkyl group is similar to that of the C₆F₅-fragment in these reactions (in contrast to previous reports).^[8,14] Although this transformation proved unselective by NMR spectroscopy, giving an alkyl vs. C₆F₅ transfer ratio of 64:36, single crystals of the product (**6**) in which the ethylbenzene group had migrated were isolated and characterised by single-crystal X-ray diffraction (Figure 2).

Although the reactions with heteroleptic boranes **1** and **2** proved unselective, they provide proof of principle that R-groups other than C₆F₅ may be transferred in the propargyl rearrangement to give novel allylboranes. It should be noted that additional reactions were conducted in which **5f** was reacted with Piers' Borane [HB(C₆F₅)₂]. In this instance rapid and clean 1,2-hydroboration of the terminal alkyne unit occurred within a few minutes, yielding the corresponding vinyl borane (**7**), indicating that the hydroboration reaction is much faster than the propargyl rearrangement.

It was found that iodoalkenylboranes (**3**) underwent more selective reactions, showing that the migratory aptitude of the vinyl group appears to be greater than that of C₆F₅. Addition of propargyl substrates (**5e-h**) to the in situ generated 1,1-carboration products (**3a,b**) in CDCl₃ showed that preferential migration of the vinyl group occurs over that of the C₆F₅-group to form the highly functionalised compounds **8a-f** (Scheme 3). The reactions were monitored by in situ multinuclear spectroscopy (¹H, ¹¹B, ¹⁹F) in which it was observed that the reaction had generally reached completion within 18 h at room temperature to give the products **8**. Evidence of the al-

ylboron product was clearly seen in the ^{11}B NMR spectra by the generation of a broad singlet at $\delta \approx 2$ ppm, indicative of these intramolecularly chelated dioxaborinine-type structures.^[19] Further evidence was obtained from the ^{19}F NMR spectra, which showed inequivalence of the fluorine atoms of the C_6F_5 -groups. The steric strain induced through the juxtaposition of the perfluorophenyl rings and the highly substituted vinyl group results in the lack of free rotation of the C_6F_5 -rings, affording ten peaks in the ^{19}F NMR instead of the expected six signals. This results in four resonances for the *ortho* fluorine atoms ($\delta = \text{ca. } -130$ to -140 ppm (6F)), three peaks for the *para* fluorine atoms ($\delta = \text{ca. } -150$ to -160 ppm, (3F)) and three resonances for the *meta* fluorine atoms ($\delta = \text{ca. } -160$ to -165 ppm (6F)).

Other characteristic features of these reactions include a singlet at $\delta = \text{ca. } 5$ ppm in the ^1H NMR spectrum, which is assigned to the C–H adjacent to boron, previously the alkynyl proton. Secondly, the quartet seen at $\delta \approx 5.5$ ppm is indicative of the vinyl proton formed as a result of the rearrangement process. Additionally, in the case of the product of the reaction between **3** and the carbamate precursor (**5h**) to yield **8f**, the characteristic exovinyl protons are clearly visible as two doublets at $\delta = 5.00$ and 4.72 ppm, respectively, in the ^1H NMR spectrum.

The products of these reactions were isolated by low-temperature crystallisation and the solid-state structures of **8a–c** and **8e–f** were determined by X-ray crystallography (Figure 3). Importantly, these structures reveal the vinylidide to be the *E*-isomer in all cases, thus elucidating the major isomer of the borane **3** as being the *E*-isomer. In addition to this, the isolated products **8a–f** present a chiral centre adjacent to boron as a result of the rearrangement step. This appears to be formed, as anticipated, in a racemic mixture of both *R* and *S* enantiomers, as confirmed by X-ray crystallographic studies. In one case, we were able to isolate a few crystals of the minor product (**9**) of the reaction in which C_6F_5 migration occurs from the reaction of **5e** with **3a**, which was confirmed by X-ray diffraction analysis (Figure 3).

An entirely different rearrangement reaction was observed in the absence of the methyl group in the propargylic position (R^2) of the esters **5a–d** (Scheme 4). When the reactions of **5a–d** ($\text{R}^2 = \text{H}$) with borane **3a** were monitored by multinuclear NMR spectroscopy, a similar chemical shift to that seen with esters **5e–g** ($\text{R}^2 = \text{Me}$) was observed in the ^{11}B NMR spectra at approximately 2 ppm, indicating a dihydrodioxaborinine structure. However, the absence of the *exo*-vinyl protons in the ^1H NMR spectrum prompted further investigation. X-ray crystallographic studies of the reaction of the *p*- NO_2 substituted ester **5d** with the vinyl borane **3a** unambiguously determined that the products of the reaction were a dimeric bis(perfluorophenyl)boranyl ester (**10a**) and the (perfluorophenylethynyl)benzene fragment (**11**) (Figure 4).

The mechanism for this reaction (Scheme 4) is presumed to proceed through activation of the propargyl position of the substrate **5** by coordination of the Lewis-acidic borane to the ester functionality of **5**. This promotes transfer of the iodide to the propargylic position, yielding propargyliodide, (perfluoro-

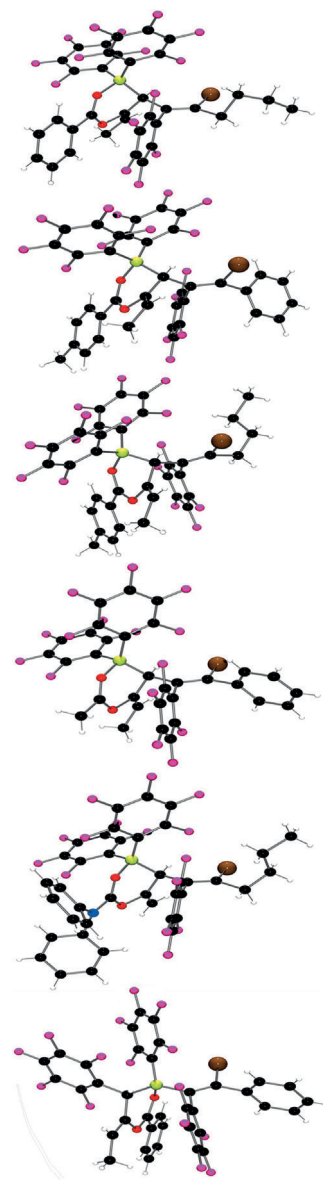
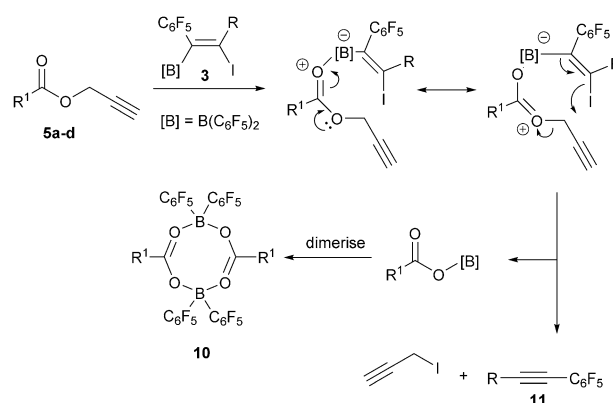


Figure 3. Solid-state structure of **8a–c**, **8e–f** and **9** (top to bottom). C: black, H: white, O: red, B: yellow-green, F: pink, I: brown, N: blue.



Scheme 4. Alternative reactivity of propargyl esters **5a–d** with vinyl boranes (**3**).

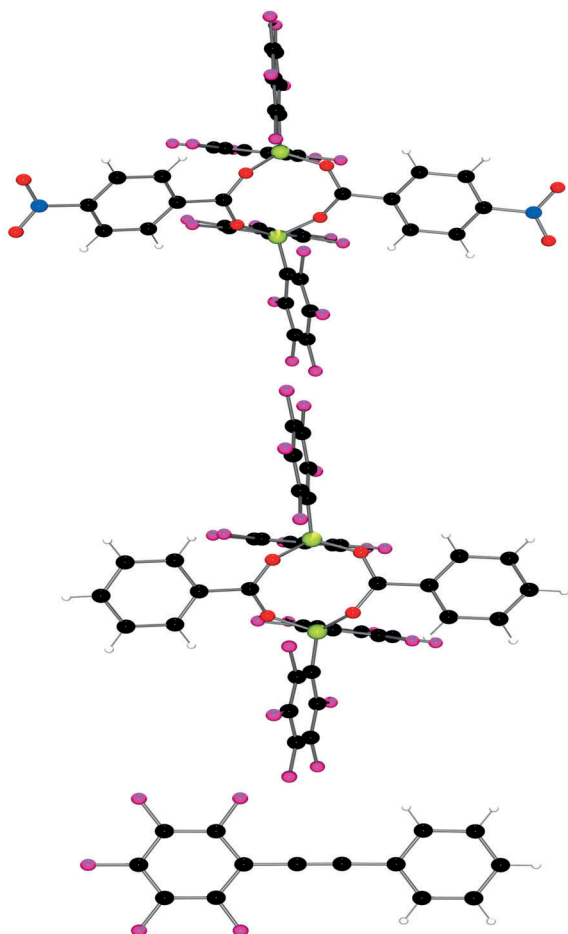
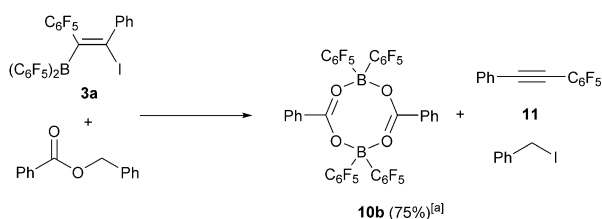


Figure 4. Solid-state structure of **10a**, **10b** and **11** (top to bottom). C: black, H: white, O: red, B: yellow-green, F: pink, N: blue.

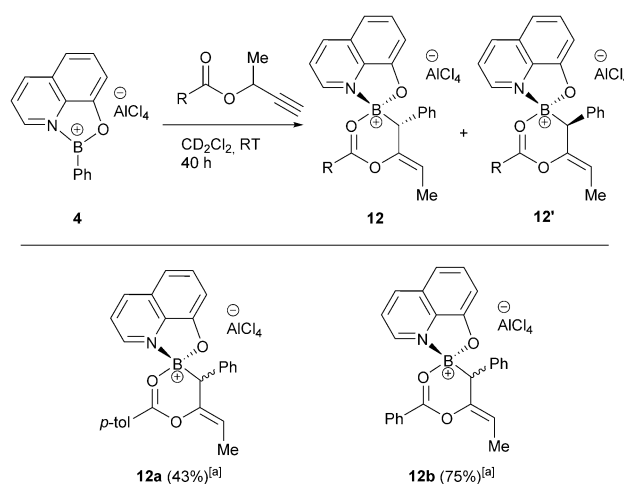
phenylethynyl)benzene (**11**) and a dimeric bis(perfluorophenyl)boranyl ester **10**, which could be isolated and characterised by X-ray diffraction (Figure 4) and observed using multinuclear NMR spectroscopy (see the Supporting Information). To test this mechanism, we reacted benzyl benzoate with the borane **3a** (Scheme 5). As expected, the products of the rearrangement could be isolated by recrystallisation and confirmed by X-ray diffraction (**10b**, **11**, Figure 4) or by ^1H NMR spectroscopy (benzyl iodide; see the Supporting Information). The divergence in this reactivity from that observed with **5e–g** is assumed to arise from the lack of steric obstruction at the propargylic posi-



Scheme 5. Reaction of **3a** with benzyl benzoate. [a] Conversion determined by in situ NMR spectroscopy.

tion, which allows for an intramolecular halide shift upon coordination of the borane to the carbonyl.

Finally, to stimulate exclusive and selective transfer of one R-group, we turned our attention to borocations, specifically the boreniums recently reported by Ingleson as transfer reagents.^[14] The 8-hydroxyquinoline (QOH) derived borenium reagent **4** was selected for the propargyl rearrangement owing to the intramolecularly coordinating nature of the quinolato ligand, which promotes exclusive transfer of the phenyl group during the reaction. Indeed, such quinolatoborenium salts have been reported by Ingleson in carboboration reactions, which demonstrated selective transfer of phenyl and (5-hexyl)thienyl groups.^[14] Upon treating the propargyl substrates **5f** with borenium (**4**) in CD_2Cl_2 , it was seen via in situ NMR spectroscopy that the expected migration of the phenyl group had occurred to give the rearranged allylboronium product **12**. As a result of this transfer step, two diastereoisomers of the product are formed in a 5:1 ratio of (*R,R*):(*R,S*) owing to the generation of a chiral boron centered *spiro*-complex (Scheme 6). A preparative scale reaction permitted single crystals of the major (*R,R*) diastereoisomer to be isolated, which were suitable for X-ray diffraction, confirming the assigned connectivity (Figure 5).



Scheme 6. Propargyl rearrangements with borenium cations (**4**). [a] Conversion to both diastereoisomers **12** and **12'** determined by in situ NMR spectroscopy.

Conclusion

In conclusion, this work has shown that a range of Lewis-acidic alkyl, vinyl and aryl boranes and borenium compounds are capable of new carbon–carbon and carbon–boron bond formation through migratory group transfer. A diverse series of heteroleptic boranes and borenium compounds have greatly expanded the formation of allyl- boron and borenium compounds beyond our initial reports. This demonstrates the fact that these Lewis-acidic boron-based compounds can lead to step-change developments in the synthetic methodology, affording novel boron and boronium compounds through com-

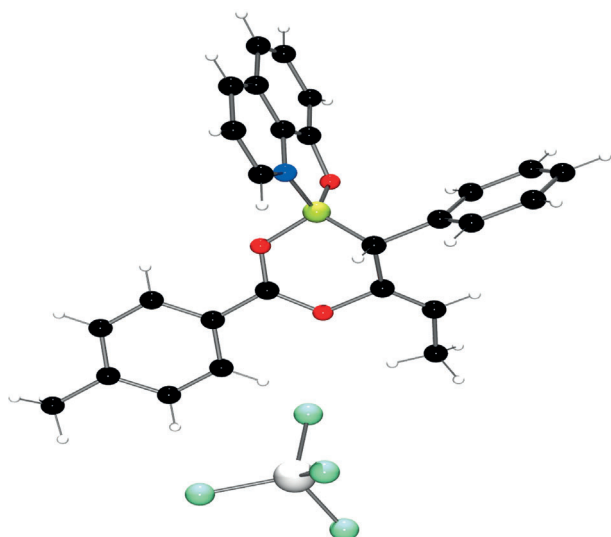


Figure 5. Solid-state structure of **12a**. C: black, H: white O: red, N: blue, B: yellow-green, Al: grey, Cl: aquamarine.

plex rearrangement reactions yielding boron substituted organic compounds with substantial molecular complexity in a one-pot reaction. The reactions of the boranes and borocations with propargyl esters results in allylboron and allylboronium species through π -activation of the alkyne followed by: 1) a 5-exo-oxoboration reaction yielding a vinyl borate and 2) subsequent ring opening with concurrent 1,2- C_6F_5 transfer from boron to carbon. In the case of $\text{PhB}(\text{C}_6\text{F}_5)_2$ (**1**) and $\text{PhCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$ (**2**), the migration reactions show reduced selectivity; however, with the vinyl boranes (**3**) and borocations (**4**), the migratory aptitude of the vinyl or phenyl group respectively is highly favoured. The methodology shown here provides a strong basis for the relative ease at which a vast library of allylboron and allylboronium compounds can be synthesised, and their widespread applications in a diverse range of fields. Indeed, these reactions lead to a novel set of allylboron and allylboronium compounds that will be of significant use to the synthetic chemist. The construction of C–C bonds through allylation and crotylation reactions have gained a prominent position as tools in organic chemistry and natural product synthesis. In the case of the selective vinyl halide migration, yet more complex functionality can be easily installed giving the products a multitude of reactive handles for subsequent transformations.

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Keywords: allylboron • borenium • borocation • carboboration • main group

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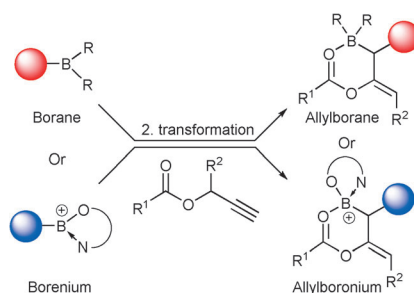
■ Boranes

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■■■ – ■■■



The Propargyl Rearrangement to Functionalised Allyl-Boron and Borocation Compounds



A diverse range of Lewis acidic alkyl, vinyl and aryl boranes and borenium compounds that are capable of new carbon–carbon bond formation through selective migratory group transfer have been synthesised. Utilising a series of heteroleptic boranes as well as borenium cations, synthetic pathways to highly functionalised, synthetically useful boron-substituted organic compounds with substantial molecular complexity have been achieved in a one-pot reaction.